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Abstract: We present an overview of laser results we obtained with Yb-doped calcium fluoride and its isotype strontium fluoride. In order to study the laser performance in femtosecond and high power regimes, spectral and thermal properties are first discussed including the potential of these crystals at room and cryogenic temperatures. Experimental demonstrations of high-power and ultrashort pulse oscillators and amplifiers are presented and analyzed.

OCIS codes: (140.3280) Laser amplifiers; (140.3380) Laser materials; (140.3480) Lasers, diode-pumped; (140.3615) Lasers, ytterbium; (320.7090) Ultrafast lasers.

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1. Introduction

Calcium fluoride (CaF_2 also known in crystallography as fluorite or fluorospar [1]), has raised the interest of the laser community since the very beginning [2,3]. Nevertheless, this matrix was almost absent for laser applications until its revival in 2004 with the ytterbium doping. Indeed, since its first laser operation in 2004 [4-6], $Yb:CaF_2$ and its isotype SrF_2 have been among the most studied and promising crystals for the development of short-pulse, high-energy, high-power diode-pumped solid state lasers [7, 8] with, for example, the recent development of a TW chain [9]. Three main reasons explain this trend. First, calcium fluoride is a simple cubic crystal whose crystallographic properties are fairly well known. This crystal can be grown in large dimension and optical-quality ceramics for laser applications have been demonstrated a long time ago [3]. Second, the simple structure of this crystal permits to obtain good thermal properties [10,11]. Finally, Yb-doped fluorides have very broad and smooth emission bands, which is exceptional for cubic crystals. This is explained by the different valencies of the dopant (Yb^{3+}) and the substituted alkaline cations (Ca^{2+}, Sr^{2+}) which induces the creation of clusters during the doping process [12-16]. The cluster organization of Yb-doped fluorides is therefore a key point to obtain ultra broad emission bands. The exceptional feature of Yb-doped fluorides, combining both good thermal and spectral properties –which are often contradictory for Yb-doped materials–, makes them very attractive (Fig. 1) for diode-pumped femtosecond solid-state lasers aiming at the generation of high-energy ultrashort pulses with high average power.

In this paper, the fluorides exception is studied more deeply with a description of the spectral and thermal properties of these materials at room and cryogenic temperatures. Moreover, the impact of these properties on laser performance is discussed by examining the experimental results already obtained in the high-average-power CW-laser regime and in ultrashort femtosecond oscillators and amplifiers.

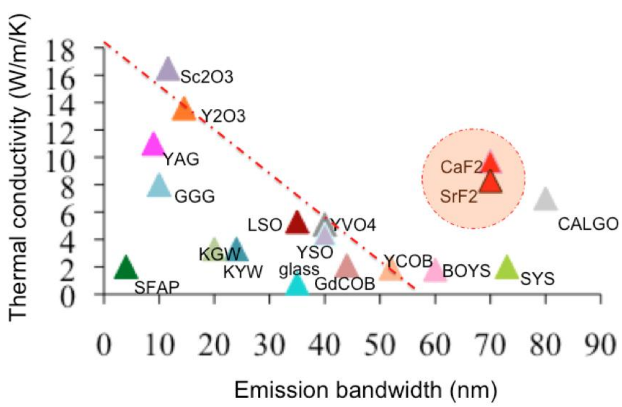

Fig. 1. Figure of merit plotting thermal conductivity (undoped crystals) versus emission bandwidth (at room temperature) in order to estimate the potential of Yb-doped laser hosts for the development of high-average-power, short-pulse lasers.

2. Spectral Considerations

One of the main spectroscopic interest of Yb-doped fluorides concerns their very broad and smooth emission bands, which is exceptional for cubic crystals. As mentioned above, it comes from the formation of Yb^{3+} clusters which occur during the doping process because of a question of charge compensation [12-16]. This cluster effect occurs at the lowest doping levels but it really becomes preponderant for Yb-doping above 0.5at%. The organization of the Yb^{3+} ions in these clusters leads to only one kind of luminescent and laser active center but due to some structural disorder inside and between the clusters, the spectroscopy of the Yb^{3+} ions resembles that of a glass leading to broad and relatively smooth absorption and emission spectra. Co-doping the crystals with charge compensating ions such as monovalent Na^+ ions has been used by some authors [17] to reduce the formation of divalent Yb^{2+} species. However, co-doping the crystals, at least by a non-negligible amount of Na^+, which was not the case in [17], would lead to a disintegration of the clusters and to an undesired change of the luminescent properties (absorption, emission and lifetime) of the lasing center, which makes the interest of this particular laser system.

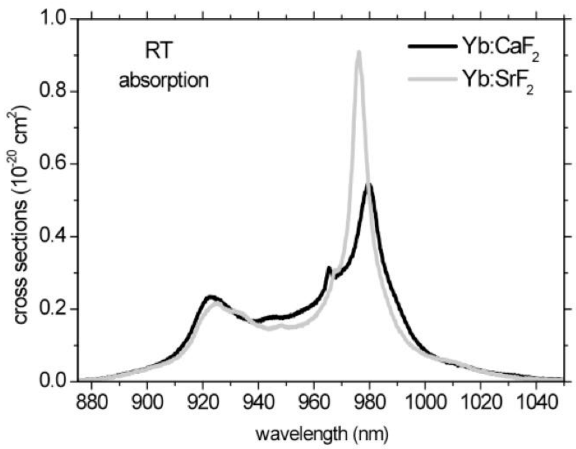

Fig. 2. Absorption spectra of $Yb:CaF_2$ and $Yb:SrF_2$ at room temperature

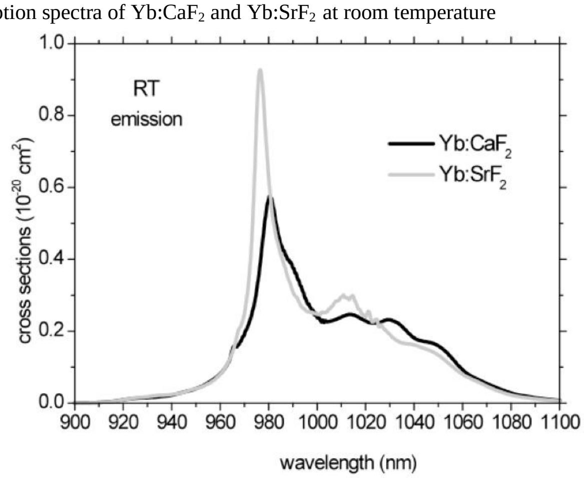

Fig. 3. Emission spectra of $Yb:CaF_2$ and $Yb:SrF_2$ at room temperature

At room temperature the spectroscopic characteristics of $Yb:CaF_2$ and $Yb:SrF_2$ are very similar (Fig. 2, 3 and 6). And at low temperature, the spectra of these two crystals slightly differ, but with the good idea of having a complementary emission spectra in the 1020-1060 nm range (Fig. 4, 5 and 6).

At cryogenic temperature (see in Fig. 4 and 5) the absorption and emission spectra are more structured but their cross sections increase and they remain sufficiently large to allow for the production of ultrashort laser pulses.

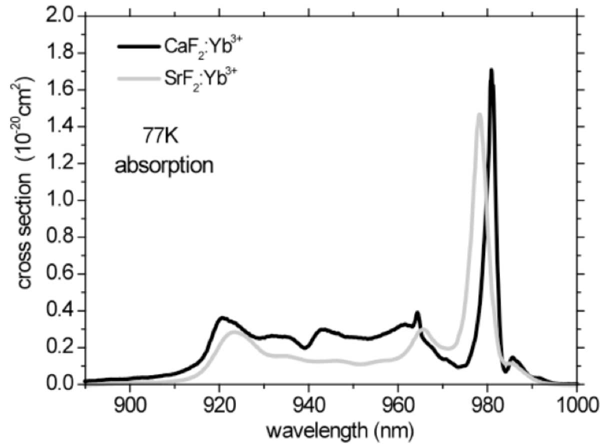

Fig. 4. Absorption spectra of Yb:CaF_2 and Yb:SrF_2 at LN2 temperature

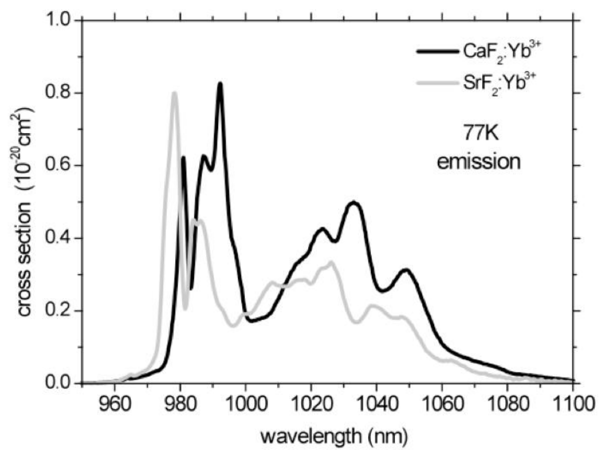

Fig. 5. Emission spectra of Yb:CaF_2 and Yb:SrF_2 at LN2 temperature

In view of these spectra and knowing their respective emission lifetimes, each material has its own advantages: a higher peak absorption cross section around 980 nm and a longer fluorescence lifetime for Yb:SrF_2 (2.9 ms compared to 2.4 ms for Yb:CaF_2), and a wider and slightly larger gain cross section spectrum (see in Fig. 6) for Yb:CaF_2.

In a regenerative amplifier configuration, the longer fluorescence lifetime is crucial since it permits higher energy storage, which leads potentially to higher energy pulses with repetition rates in the 100 Hz range. However, for mode-locked operation, the long lifetime becomes a disadvantage, leading to a strong tendency to operate in Q-switched regime [18]. It is also interesting to notice that the Yb:SrF_2 gain cross-section spectrum is shifted to shorter wavelengths compared to the Yb:CaF_2 spectrum. This spectral complementarity might be useful to design ultra broad laser oscillators and amplifiers based on the combination of both materials.

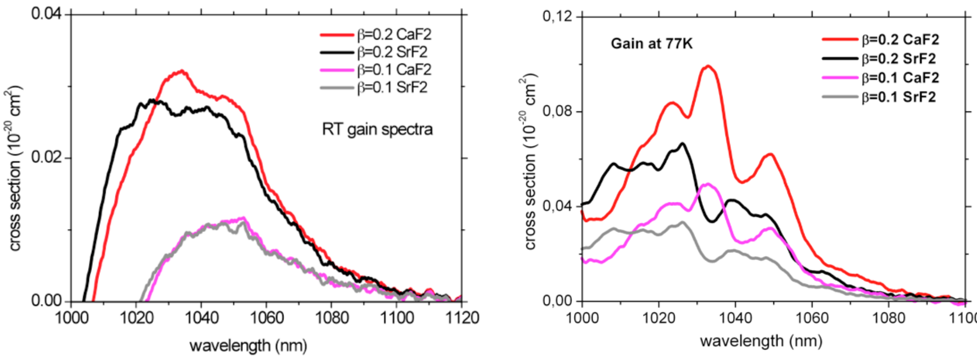

Fig. 6. Gain cross section of Yb:CaF_2, and Yb:SrF_2 (for beta= 0.1 and 0.2) at room temperature (left) and LN2 temperature (right)

3. Thermal Considerations

At first glance, the thermal properties and especially the thermal conductivities of calcium fluoride and strontium fluoride seem well-suited to the design of high power lasers. Indeed, the relatively simple structure of these cubic crystals induces good thermal conductivities in the range of 10 $W.m^{-1}K^{-1}$ at room temperature: 9.7 $W.m^{-1}K^{-1}$ for undoped CaF_2 and 8.3 $W.m^{-1}K^{-1}$ for undoped SrF_2. Nevertheless, other thermal properties of materials must be taken into account to assess more precisely their potential for high power lasers.

Specifically, a second important parameter is the thermo-optic coefficient. This parameter results from three effects: the refractive index variation versus temperature (dn/dT), the thermal expansion of the crystal, and the mechanical stress induced by the thermal loads. In the case of CaF_2 and SrF_2 [11] the second term is positive while the two others are negative with approximately the same absolute value, resulting in a negative thermo-optic coefficient of $-11.3x10^{-6}$ K^{-1} for CaF_2 and $-15.9x10^{-6}$ K^{-1} for SrF_2 at room temperature. The thermal lenses induced in the fluorides are relatively small and negative, making these crystals quite atypical compared to others whose thermo-optic coefficients are quasi systematically positive (e.g. in YAG the thermo-optic coefficient is $8.9x10^{-6}$ K^{-1}).

Another important thermal properties is the thermal shock parameter [19,20]; it is well known that fluorite is sensitive to thermal shocks. Indeed, the thermal shock parameter of undoped CaF_2 (cf. table 1) is 7 times lower than for YAG for example. Fluorite is therefore relatively sensitive to fracture, and requires special precaution in high power pumping configuration to ensure slow variations of pump power absorption.

Concerning parasitic thermal loads, a strong advantage of CaF_2 is its broad transparency range extending up into the VUV (≈160 nm), which avoids the possibility of multi-photon absorptions at high power levels. Nevertheless, when doped with ytterbium, the crystal transparency range depends strongly on the growing process. Indeed, depending on the fabrication technique, the possible presence of Yb^{2+} leads to an absorption band around 390 nm (Fig. 7). To avoid the formation of divalent Yb^{2+} species, it is not necessary to co-dope the crystals with charge compensators like Na^+ or to apply special post-growth treatment. Actually, it is only necessary to grow the crystals with the adequate atmosphere. The overall thermal behavior can be degraded under high intensity pumping if the quantity of Yb^{2+} is not adequately reduced. Moreover, the growing process of Yb:CaF_2 and Yb:SrF_2 is sufficiently well mastered to allow a very good quantum efficiency (determined with the method of Chénais et al. [21-23]): measured to be higher than 99% in both cases. This leads to a very low thermal load due to non-radiative effects with these crystals: 0.7 % for Yb:CaF_2 and 0.5 % forYb:SrF_2.

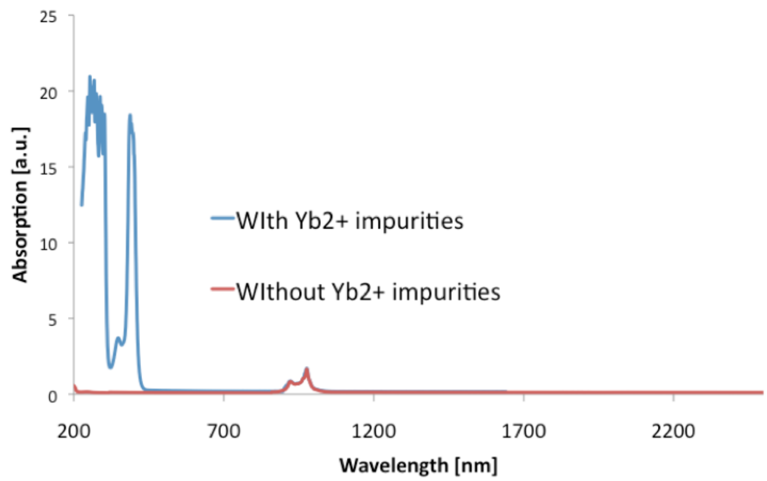

Fig. 7. Absorption spectra for two different qualities of Yb:CaF_2 crystals.

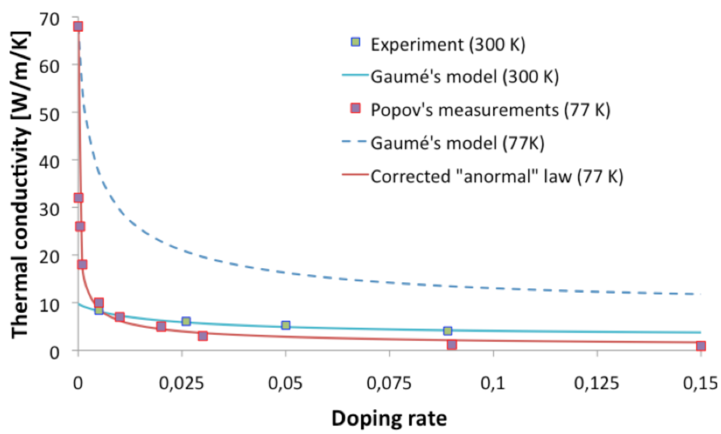

Fig. 8. Thermal conductivity versus doping level (Yb/Ca) for Yb:CaF_2 at room and LN_2 temperatures [10,24-26].

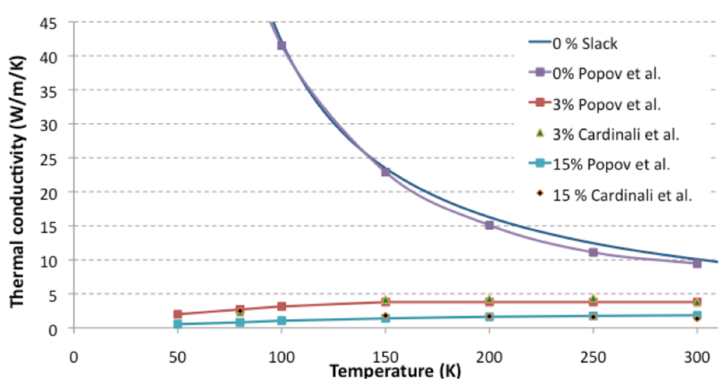

Fig. 9. Thermal conductivity versus temperature (Yb/Ca) for Yb:CaF_2 for 0%, 3 % and 15 % doping levels [10,24-26].

Table 1. Spectroscopic and thermal properties of undoped and Yb doped CaF_2 at room and LN_2 temperatures [6,10,11,19, 25, 27-33]

Undoped crystal	CaF_2 At 273 K	CaF_2 At 77 K
Thermal conductivity ($W\ m^{-1}K^{-1}$)	9.7	68
Hardness (Knoop : kg/mm^2)	140-160	
(Moh)	4	
Elastic compliance (1/TPa) : s_{11}	6.83	
s_{12}	-1.46	
s_{44}	29.6	
Elastic moduli (GPa) : c_{11}	165.3	
c_{12}	44.5	
c_{44}	33.8	
Young Modulus (GPa) : <100>	146.4	
<111>	89.6	
Poisson ration ν	0.21	
Linear thermal expansion ($10^{-6}\ K^{-1}$)	18.9	4.5
Vickers Hardness (GPa)	2	
Fracture toughness ($MPa\ m^{1/2}$)	0.7	
Tensile fracture strength (optically polished) (MPa)	157	
Thermal shock parameter ($W\ m^{-1}$)	436	12800*
Melting point	1691 K	
Elasto-optic coefficient: p_{11}	0.089	
p_{12}	0.223	
p_{44}	0.024	
dn/dT ($10^{-6}\ K^{-1}$)	-11.3	-3
χ dilatation ($10^{-6}\ K^{-1}$)	10.3	2.46
χ stress ($10^{-6}\ K^{-1}$)	-11	-2.62
Thermo-optic coefficient ($10^{-6}\ K^{-1}$)	-11.3	-3.16
Sound velocity (m/s)	5870	
Refractive index n (@ λ=1μm)	1.429	1.435
Non-linear index n_2, ($10^{-20} m^2/W$)	1.9	
Doped crystal ≈2.5%	**$Yb:CaF_2$ At 273 K**	**$Yb:CaF_2$ At 77 K**
Standard laser wavelength λ_L (nm)	1053	1034
Standard absorption wavelength λ_P (nm)	979.6	980.9
Absorption cross section @ λ_P ($10^{-20}\ cm^2$)	0.54	1.7
Emission cross section @ λ_L ($10^{-20}\ cm^2$)	0.16	0.49
Absorption cross section @ λ_L= ($10^{-20}\ cm^2$)	0.0029	0.00066
Emission cross section @ λ_P ($10^{-20}\ cm^2$)	0.48	0.62
Mean fluorescence wavelength (nm)	1005	1018
Fluorescence lifetime	2.4	
$I_L$sat ($kW.cm^{-2}$)	32	17
Thermal conductivity ($W\ .m^{-1}.K^{-1}$)	5.4	4.9
Thermal shock parameter ($W\ m^{-1}$)	242*	925*
Thermo-optic coefficient ($10^{-6}\ K^{-1}$)		
In situ measurements	-17.8	-2.45

* Calculated taking into account the value of the parameters at 77 K when found in the literature.

Another effect to take into account to fully assess the thermal properties is the influence of the Yb^{3+} doping on the thermal behavior.

Up to now, few works have been performed on this subject. But it clearly appears that the doping level impacts negatively the thermal properties. For example, the thermal conductivity decreases by a factor of 2 from undoped CaF_2 to 5%Yb- doped CaF_2. To approximate the behavior, a law for low doping level (< 10 %), derived from the Gaumé's model[24], is given by the following equation:

$$\kappa = \beta\sqrt{\frac{\kappa_0}{d}}\ \arctan\left(\frac{\sqrt{\kappa_0 d}}{\beta}\right), \qquad (1)$$

where κ_0 stands for the thermal conductivity for the undoped crystal, d the doping level [34], and β equals at room temperature to 0.28 for $Yb:CaF_2$ and 0.15 for SrF_2. In conclusion the doping level strongly influences the thermal properties. The change of thermal conductivity also affects other thermal properties, such as the thermal shock parameter, which is proportional to the thermal conductivity.

One way to improve the thermal properties of Yb-doped laser crystals like $Yb:CaF_2$, is to decrease the temperature [35-36]. Indeed, in general, thermal properties, such as thermal expansion, thermal conductivity and thermo-optic coefficient can be significantly improved by reducing the temperature. For example, in the case of undoped CaF_2, the thermal conductivity increases by a factor of 7 by lowering the temperature down to 77 K (see in table 1). Following Slack measurements [10], the thermal conductivity increases hyperbolically down to about 50 K according to an empirical law given by $\kappa_0 = 2652\ /(T - 37)$. In parallel, the thermal expansion of undoped CaF_2 decreases by a factor 4.2 and its thermo-optic coefficient by a factor 3.6 by lowering the temperature down to 77 K. Such behaviors thus really improve the thermal properties of the crystals; for instance, they improve their resistance to the thermal shocks by about a factor of 30. However, when the crystals are doped with rare-earth ions like Yb^{3+}, the situation may greatly change. For example, according to Popov and Cardinali's measurements [25,26] (Fig. 8 and 9) the behavior of the thermal conductivity of heavily doped $Yb:CaF_2$ seems to be very particular, since it is decreasing (instead of increasing) by lowering the temperature, which is typical of disordered systems but is anomalous for crystals of simple stoichiometric composition. In fact, in the case of $Yb:CaF_2$, the thermal conductivity only increases for low (<0.1%Yb) dopant concentrations and it stays nearly constant for about 1%Yb dopant concentrations. Such particular behavior is to be related with the clustering of the Yb^{3+} ions, which occurs at high dopant concentrations, and the resulting effect on the mean-free path of the phonons in this material. As a consequence, the β parameter which enters in equation (1) cannot be considered, as expected for a standard crystal, as a constant; actually, at 77 K, this factor drastically drops down to 0.05 for $Yb:CaF_2$. With this consideration, the thermal properties at low temperature consist in a trade off between the different thermal parameters. Nevertheless, if we consider the thermal shock parameter as a real factor of merit, the lowering of the temperature still remains beneficial but only by a factor 3.8 for a 3%Yb doped crystal.

Other drawbacks associated with low temperature operation are related to spectroscopic considerations: the emission spectrum consists of sharper features and the average fluorescence wavelength is longer, leading to an increase of the thermal load due to fluorescence by 50 %.

In conclusion, laser operation at cryogenic temperature has to be considered very precisely; in fact the pros are higher gain and better thermal resistance at high power level but the cons are the more structured emission band and a strong dependence of the thermal conductivity with the doping concentration.

4. High Power Experiments

To validate the good thermal properties of fluorides and especially of $Yb:CaF_2$, high power laser experiments have been performed in the CW regime [11]. At room temperature, with a simple 3-mirror cavity operating in the TEM00 mode, with a 2.6-%Yb-doped 5-mm long

$Yb:CaF_2$ crystal, 10.2 W at 1053 nm have been obtained for a 64 W incident pump power at 980 nm (39 W absorbed) and, with a 2.9-%Yb-doped 5-mm long $Yb:SrF_2$ crystal, 5.8 W at 1051 nm have been obtained for 26 W incident power (20 W absorbed). In these conditions the temperature difference between the center of the laser beam in the crystal and the periphery is around 30°C, leading to a thermal lens with a focal length around -110 mm. At cryogenic temperature (77 K), the laser performances are clearly improved [37]: a total average power of 97 W at 1034 nm is obtained when pumping with 212 W incident power (150 W absorbed). These better performances can be explained first by the increase of the gain cross section which allows a better laser efficiency; and also by the possibility of pumping with higher pump power. Actually, the better thermal shock parameter at cryogenic temperature allows us to pump up to 250 W instead of 100 W which was, at room temperature, closed to the fracture limitation with our apparatus.

5. Short Pulse Generation

In order to generate the shortest pulse, we used the cavity described in Fig. 10 with a high brightness laser diode: a 7-W laser diode at 980 nm coupled to a 50 μm fiber. We used 6.1-mm-long, 3 x 7 mm^2 section Brewster-cut crystals : an $Yb:CaF_2$ crystal doped at 2.6 % and an $Yb:SrF_2$ crystal doped at 2.9 % [38-39]. The repetition rate of the cavity was 112.5 MHz.

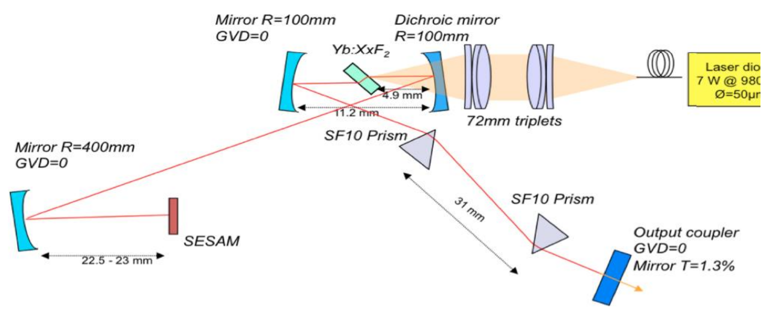

Fig. 10. Short-pulse oscillator setup.

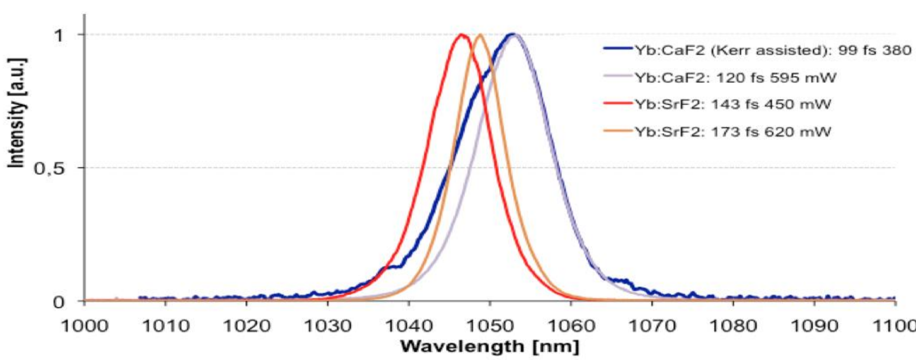

Fig. 11. Spectra obtained with in mode-locked oscillator.

The shortest pulses are obtained with $Yb:CaF_2$. We achieve a stable continuous-wave modelocked (CW ML) regime with 99 fs pulses. The average power is 380 mW for a 7 W pumping diode. The corresponding spectrum is centred at 1053.4 nm (Fig. 11) and has a bandwidth of 13.2 nm. In this case the short pulses are generated with the assistance of the

Kerr effect. The non-linear index of CaF_2 is 1.9×10^{-20} m^2/W [40]. The spectrum is clearly broadened compared to the case where the Kerr effect is negligible (Fig. 11): in this case, the pulse is lengthened (120 fs) and the power gets higher (595 mW).

For $Yb:SrF_2$ the pulses are longer but the average power gets higher. The shortest pulses obtained with this setup have a duration of 143 fs for a 8.5-nm-bandwidth spectrum centered at 1046.7 nm. The corresponding average power is 450 mW. The long lifetime of $Yb:SrF_2$ does not favor mode-locking[18] and a soliton-like regime [41] strongly assisted by the SESAM absorber [42] is then expected. Soliton pulse shaping and gain filtering play a major role in obtaining a stable mode-locked regime. Therefore small deviations from the ideal soliton regime would result in energy shedding to continuum, thereby initiating Q-switching for this long lifetime material. In other words, the range of stable CW-ML operation around the “ideal” soliton regime is very restricted [43]. Moreover the Kerr lens effect is smaller in the case of SrF_2 where the non-linear index equals 1.76×10^{-20} m^2/W [40]. The experimentally obtained time-bandwidth product reflects this ideal soliton regime with a value only 5% above the theoretical value.

In conclusion, $Yb:CaF_2$ seems more favorable than $Yb:SrF_2$, in the same conditions, to generate short pulses. Nevertheless, the emission spectra are slightly different which can justified the use of $Yb:SrF_2$ for some specific applications. Compared to other crystals[44], the potential for ultrashort pulse duration seems not fully exploited for $Yb:CaF_2$ and $Yb:SrF_2$. Nevertheless they have demonstrated good performances in terms of pulse duration and average power for femtosecond oscillators in the 1050 nm range.

6. Short Pulse Amplification

To evaluate the performance of fluoride crystals in amplifiers, a regenerative amplifier has been developed with the main goal of exploring the limitations in terms of pulse duration of $Yb:CaF_2$ and $Yb:SrF_2$ based amplifiers [45]. The experiment was performed with the same crystals used for the oscillators. The experimental set-up for the regenerative amplifier is illustrated in Fig. 12. In order to optimize the injection spectrum in terms of bandwidth and maximum gain, the seed pulses were generated by a broadband Yb:CALGO oscillator centered at 1043 nm with a fwhm bandwidth of 15 nm at a repetition rate of 27 MHz [46]. The pulses are stretched to 260 ps with a single transmission grating (1600 l/mm) optical arrangement. The regenerative amplifier is composed of a thin-film polarizer (TFP) and a BBO Pockels cell. The Pockels cell is adjusted as a quarter waveplate at 45° in the static state, i.e. without high voltage, and no birefringent effect with high voltage. The TFP is used in combination with the Pockels cell to extract the output pulse. Between the stretcher and the amplifier, a TFP, a Faraday rotator and a half-wave plate are used to separate the input and output beams. Finally, after increasing the beam diameter by a factor of two, the chirped pulses are sent to a grating compressor (1600 l/mm), based on two transmission gratings, with a 45% efficiency.

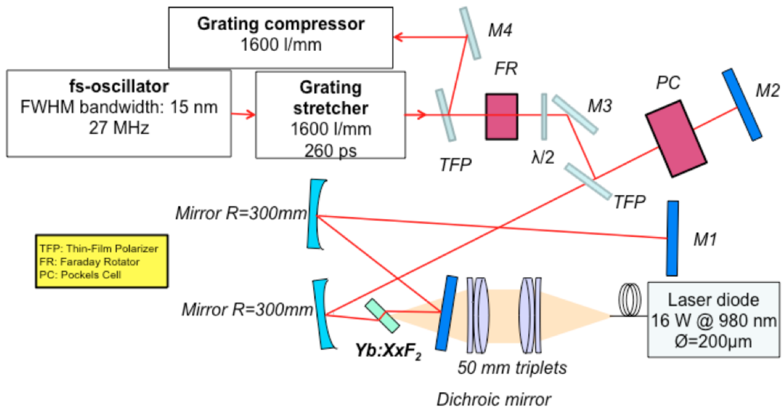

Fig. 12. Regenerative amplifier setup

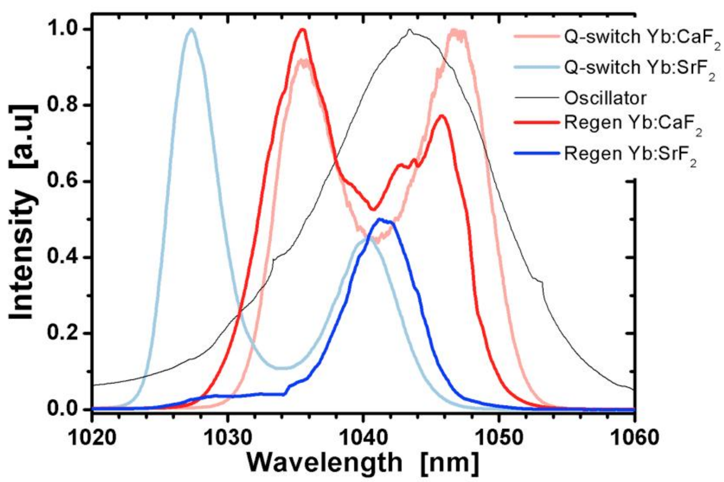

Fig. 13. Evolution of the spectrum in Q-switched and injected regime (blue and deep blue for $Yb:SrF_2$, red and deep red for $Yb:SrF_2$-), and oscillator spectrum (black)

As shown in Fig. 13, with $Yb:CaF_2$, when the seed pulse is centered at 1043 nm, the bandwidth of the output pulse is 15 nm, fitting well with the spectrum obtained in the Q-switched free running mode. The input spectrum (centered at 1043 nm) is slightly blue-shifted to 1040 nm, corresponding to the gain spectrum of $Yb:CaF_2$. At repetition rates up to 500 Hz, a pulse energy of 1.4 mJ/0.62 mJ (before/after compression) with a pulse duration of 178 fs is obtained.

With $Yb:SrF_2$, at a 100 Hz repetition rate, we obtain a pulse duration of 325 fs for a spectral bandwidth of 5.8 nm (FWHM). The energies before and after compression are 1.4 mJ and 850 µJ respectively, giving an-optical-to-optical efficiency of 1.1% before compression. The build-up time in the present case is 1.7 µs compared to 1.4 µs in the case of $Yb:CaF_2$ indicating a lower small single pass gain. Shorter pulses are obtained with $Yb:CaF_2$, but this is mainly due to the better overlap between the Yb:CALGO oscillator and the $Yb:CaF_2$ gain spectra. Indeed, the $Yb:SrF_2$ gain spectrum is shifted to shorter wavelengths, and only one peak of the Q-swiched free-running-mode spectrum is used efficiently.

An interesting aspect of these results is that spectra obtained with $Yb:CaF_2$ and $Yb:SrF_2$ are remarkably complementary. Both spectra have a “camel” shape, i.e. peaks located at 1027 and 1041 nm and a dip at 1036 nm for $Yb:SrF_2$, and peaks at 1036 and 1047 nm and a dip at

1041 nm for Yb:CaF_2. Thus, by combining both materials (with two different bulk crystals or single combined ceramics [47]) we should obtain a broadband gain spectrum between 1025 and 1050 nm. Seeded by a broadband oscillator, with a spectrum centered at 1038 nm, a regenerative amplifier with both crystals in the cavity should lead to sub-100 fs laser pulses, with the potential for a few millijoules pulses at a high repetition rate.

The interest of Yb:CaF_2 and Yb:SrF_2 compared to other Yb-doped crystals are much more obvious for amplifiers[48] than for oscillators. In fact, in the current state of the art, they are among the best Yb-doped crystals for short pulse duration [45,49] and high peak power [9] generation tanks to their exceptional bandwidth and storage capacity.

7. Conclusion

The potential of ytterbium-doped calcium and strontium fluorides for high-power short pulse lasers has been demonstrated. Multi-watt oscillators and amplifiers have been developed successfully. This is due to the very particular spectroscopic and thermal properties of this crystal family, combining ultra-broad emission bandwidths and good thermal properties. The values of various physical parameters that are relevant for high-power short pulse operation clearly confirm the attractiveness of this material for laser applications. The experiments presented in this paper represent a summary of the work done by the CIMAP and LCFIO laboratories. For a more complete state of the art, the authors would like to point out other very interesting works made at the Institute for Optics and Quantum Electronics (Jena) within the POLARIS Project and the Research Center Dresden-Rossendorf (FZD Dresden) within the FZD-Petawatt Project on high-energy diode-pumped solid state lasers based on Yb:CaF_2 and Yb:SrF_2 [7,9,50-51], at the Photonics Institute of Vienna on short pulse amplifiers at cryogenic temperature based on Yb,Na:CaF_2 and Yb:CaF_2 [17,49,52] and at the Laser Materials and Technology Research Center (Russia) on doped fluoride crystals and ceramics [53-54] associated with the Bryansk State University (Russia) for the thermal properties studies [25,55-57]. The field of applications of fluorides is then in full expansion. The current developments now concern the scaling up in energy involving studies on high-quality, large-dimension crystals [58-59], the scaling up in average power involving specific laser geometries such as thin disks [60-62], slabs [63] and crystalline fibers [64], and the short pulse operation at cryogenic temperature involving ultra-low quantum defect configuration [65].

8. Acknowledgments

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